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## Electrical conduction in lead–iron glasses

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**Abstract.** Temperature and compositional dependences of electrical conductivity in lead–iron glasses are reported. The experimental results are analysed in the light of existing theories. It has been observed that the electrical conduction in these glass compositions at high temperatures is best described by Mott's phonon-assisted hopping model, while the low-temperature data are consistent with the variable-range hopping model. Hopping at high temperatures occurs in the non-adiabatic regime. The generalized hopping model of Schnakenberg is the best to interpret the temperature dependences of the conductivity and activation energy over the glass compositions studied. Values of the physical parameters obtained by the best fits of the experimental data are consistent with the glass compositions.

### 1. Introduction

Oxide glasses containing transition metal (TM) ions, such as V and Fe are of considerable interest because of their potential applications as memory switching devices [1] or ferrites [2]. Electrical conduction processes in glasses containing vanadium ions have been more extensively studied than other TM ions such as Fe [3–8]. Electrical conduction in TM oxide glasses has been ascribed to the hopping of polarons between two different valence states of the TM ions [4, 5]. However, there are few reports [7] on the TM ion glasses prepared with non-conventional network formers such as PbO or Bi<sub>2</sub>O<sub>3</sub>. These non-conventional glasses are also of particular interest, because they can be used to produce glass–ceramics, layers for optoelectronic devices, thermal and mechanical sensors, etc [9, 10]. A few studies [11–13] on oxide glasses containing iron ions have showed that iron ions in these glasses form clusters which exhibit superparamagnetic behaviour. Below the freezing temperature, individual spins are frozen in random directions because of an antiferromagnetic interaction between nearby ions [11, 12]. The purpose of the present work is to study the composition and temperature dependences of the electrical properties of non-conventional PbO–Fe<sub>2</sub>O<sub>3</sub> glass.

### 2. Experimental procedure

Glass samples of different compositions (PbO)<sub>100-x</sub>(Fe<sub>2</sub>O<sub>3</sub>)<sub>x</sub> with  $x = 5\text{--}25$  mol% were prepared from reagent-grade chemicals. Calculated amounts of PbO and Fe<sub>2</sub>O<sub>3</sub> (table 1) were mixed and melted in pure alumina crucibles. The melts were kept for 2 h at a temperature in the range 1000–1200 °C depending on composition. The melts were finally either poured in a twin roller or pressed between two brass plates to form the glass samples. The amorphous nature of the samples were confirmed by x-ray diffraction, differential

thermal analysis, scanning electron microscopy and infrared spectroscopic study. The results of these studies have been reported in detail elsewhere [14]. The final chemical compositions of the glass samples, the concentrations  $N$  of total iron ions and the concentrations of  $\text{Fe}^{2+}$  ions were determined by redox titration using the procedure reported earlier [8]. The densities of the samples were measured using Archimedes' principle. The average intersite separation  $R$  between Fe ions was obtained from the estimated glass compositions. The estimated glass compositions, the concentrations of total and reduced iron ions, the ratio  $C$  of the reduced iron ion to the total iron ion concentrations, the average intersite separations between iron ions, the densities and the glass transition temperatures determined from DTA are shown in table 1. Electrical contact was made using gold electrodes, deposited by vacuum evaporation. The gold-coated samples were heat treated at  $150^\circ\text{C}$  for 2 h. The absence of barrier layers at the contacts was confirmed by the linear  $I$ - $V$  characteristics. Measurements were carried out using a Keithley (model 617) electrometer in the temperature range 210–550 K.

**Table 1.** Estimated glass compositions, densities, concentrations  $N$  of the total Fe ions, concentrations  $[\text{Fe}^{2+}]$  of reduced iron ions, ratios  $C = [\text{Fe}^{2+}]/N$ , intersite separations  $R$  and glass transition temperatures  $T_g$  of lead-iron glasses.

Glass composition (mol%)		Density ( $\text{g cm}^{-3}$ )	$N$ ( $10^{22} \text{ cm}^{-3}$ )	$[\text{Fe}^{2+}]$ ( $10^{19} \text{ cm}^{-3}$ )	$C = [\text{Fe}^{2+}]/N$	$R$ ( $\text{\AA}$ )	$T_g$ ( $^\circ\text{C}$ )
$\text{Fe}_2\text{O}_3$	$\text{PbO}$						
28	72	7.20	1.18	7.39	0.006	4.39	320
19	81	7.21	0.78	2.99	0.008	5.04	360
9	91	7.23	0.36	4.40	0.012	6.54	370
5	95	7.24	0.20	3.02	0.015	7.99	380

### 3. Results and discussion

The electrical DC conductivity as a function of inverse temperature for several glass compositions is shown in figure 1. The figure shows that the logarithmic conductivity varies non-linearly at lower temperatures. The non-linearity decreases with decrease in the iron ion concentration in the glass samples. This change in activation energy with temperature is a clear indication of small-polaron hopping conduction [3, 4, 15, 16]. In the high-temperature region the variation in activation energy with temperature is small so that the behaviour may be treated as activated. The variation in conductivity at 400 K and activation energy with composition is shown in figure 2. The above results are analysed in the light of small-polaron hopping theories.

Different theories have been proposed for electrical conduction in glassy semiconductors. Only those theories which fit our experimental data fairly well will be discussed here. Mott [3] has investigated theoretically the hopping conduction in TM oxide glasses. The conduction process has been described as the phonon-assisted hopping of a small polaron between localized states (i.e. two different valence states of TM ions). The following expression has been obtained for the nearest-neighbour hopping in the non-adiabatic regime at high temperatures ( $T > \Theta_D/2$ ):

$$\sigma = \nu_o [e^2 C(1 - C)/k_B T R] \exp(-2\alpha R) \exp(W/k_B T) \quad (1)$$

where  $\nu_o$  is the optical phonon frequency,  $\alpha^{-1}$  is the localization length of the s-like wavefunction assumed to describe the localized states at each TM ion site,  $R$  is the average

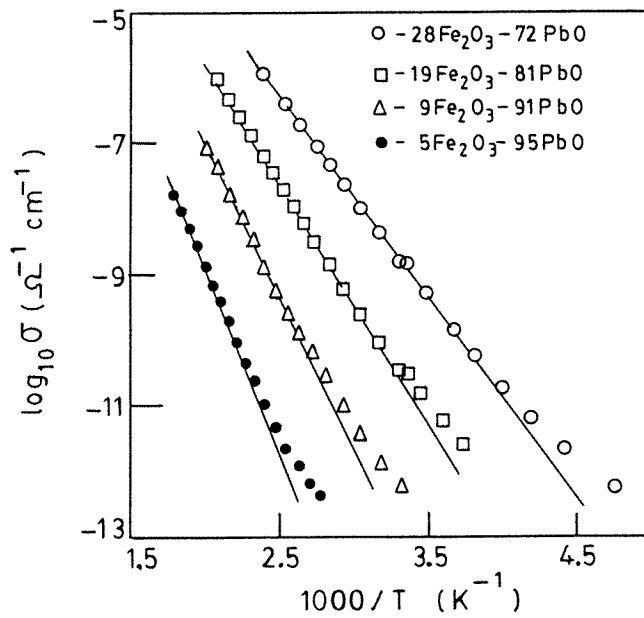


Figure 1. Temperature dependences of conductivity for several lead-iron glasses: —, best fits to equation (1).

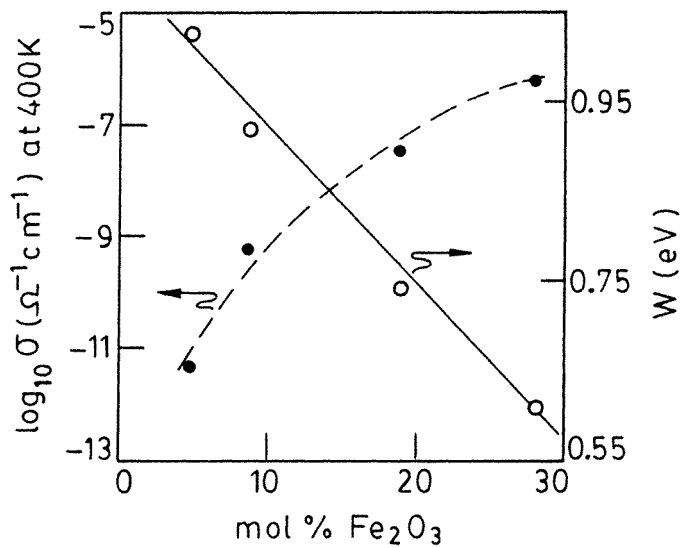


Figure 2. The variations in activation energy (○) and conductivity (●) at 400 K with composition.

intersite separation of the TM ions,  $C$  is the fraction of sites occupied by an electron or polaron and is therefore the ratio of the TM ion concentration in the low valence states to the total TM ion concentration and  $W$  is the activation energy for the hopping conduction.

Assuming strong electron–phonon interaction, Austin and Mott [4] have shown that

$$W = \begin{cases} W_H + W_D/2 \\ W_D \end{cases} \quad \text{for} \quad \begin{cases} T > \Theta_D/2 \\ T < \Theta_D/4 \end{cases} \quad (2)$$

where  $W_H$  is the polaron hopping energy,  $W_D$  is the disorder energy arising from the variation in local environment of the ions and  $\Theta_D$  is the Debye temperature defined by  $h\nu_o = k_B\Theta_D$ .

Our conductivity data above 320 K can be interpreted consistently using this model. In figure 1, equation (1) is fitted to the experimental data by the least-squares fitting procedure. The best fits are observed for the values of parameters shown in table 2. In the calculation, estimated values of  $\nu_o$  from infrared spectra [14] were used. It may be noted that the values of  $W$  decrease with increase in  $\text{Fe}_2\text{O}_3$  content in the glass. The values of  $\alpha$  are also reasonable for strong localization in the present glass system [4]. It is also noted that the values of  $\alpha$  increase with increase in the  $\text{Fe}_2\text{O}_3$  content in the glass compositions.

**Table 2.** The values of the parameters obtained from the best fits of Mott's phonon-assisted hopping model and the variable-range hopping model to the experimental data.

$\text{Fe}_2\text{O}_3$ (mol%)	$r_p$ (Å)	$\alpha$ (Å <sup>-1</sup> )	$\nu_o^a$ (10 <sup>13</sup> s <sup>-1</sup> )	$W$ (eV)	$N(E_F)$ (10 <sup>18</sup> eV <sup>-1</sup> cm <sup>-3</sup> )
28	1.768	0.142	0.88	0.64	3.63
19	2.032	0.138	1.00	0.78	2.55
9	2.634	0.136	1.10	0.96	1.63
5	3.219	0.119	1.20	1.08	0.83

<sup>a</sup> From [14].

An estimation of the polaron radius can be obtained from the following formula derived by Bogomolov *et al* [17] for the case of a non-dispersive system of frequency  $\nu_o$ :

$$r_p = (\pi/6)^{1/3}(R/2). \quad (3)$$

The estimate of  $r_p$  from equation (3) using the values of  $R$  from table 1 are shown in table 2. The small values of  $r_p$  also confirm the strong localization in the glass compositions [4].

It has been shown [5, 18] that the nature of the hopping mechanism can be predicted from the plot of the logarithmic conductivity versus activation energy at an experimental temperature for all glass compositions. It has been suggested [5] that, if the temperature estimated from the slope of this plot is close to the experimental temperature, then the hopping will be in the adiabatic regime; otherwise it will be in the non-adiabatic regime. For the lead–iron glasses a plot of logarithmic conductivity at 400 K versus activation energy is shown in figure 3. It is clear that the plot is not linear and the estimation of temperature from this is not possible; thus the nature of hopping mechanism for these glass compositions cannot be concluded from this plot. This is because the conductivity decreases rapidly with decrease in the  $\text{Fe}_2\text{O}_3$  content in the glass and the activation energy alone cannot control the conductivity. However, the polaron hopping model proposed in [15] gives an independent way to check the nature of the hopping mechanism. The criterion for the nature of hopping is

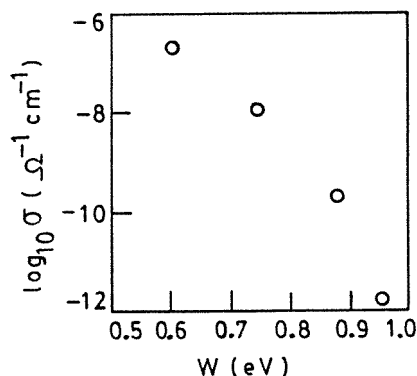
$$J \gtrless (2k_B T W_H/\pi)^{1/4} (h\nu_o/\pi)^{1/2} \quad (4)$$

where  $J$  is the polaron band width related to electron wavefunction overlap on adjacent sites, and  $>$  and  $<$  indicate adiabatic and non-adiabatic hopping, respectively. The condition for

formation of a small polaron is also given by  $J < W_H/3$ . Limiting value of  $J$  is estimated from expression (4) using the values of  $W_H \approx W$  (table 2) and is found to lie within the range 0.035–0.052 eV for all compositions. An estimate of  $J$  can be made following the expression [19]

$$J \simeq e^3 [N(E_F)/\epsilon_p^3]^{1/2} \quad (5)$$

where  $\epsilon_p$  is the effective dielectric constant. Employing the values of  $N(E_F)$  from table 3, equation (5) gives  $J = 0.001$ – $0.003$  eV depending on composition, and thus hopping in these glasses occurs in the non-adiabatic regime.



**Figure 3.** The variation in logarithmic conductivity at 400 K with activation energy for the lead-iron glasses.

**Table 3.** Parameters obtained from the best fits of Schnakenberg's generalized polaron hopping model to the experimental data.

Fe <sub>2</sub> O <sub>3</sub> (mol%)	$\nu_0$ (10 <sup>13</sup> s <sup>-1</sup> )	$W_H$ (eV)	$W_D$ (eV)
28	0.93	0.64	0.09
19	1.04	0.76	0.08
9	1.19	0.90	0.08
5	1.31	1.10	0.05

At lower temperatures ( $T < \Theta_D/4$ ), Mott [20] has proposed that hopping may occur preferentially beyond nearest neighbours. The conductivity for this variable-range hopping is proposed to be

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad (6)$$

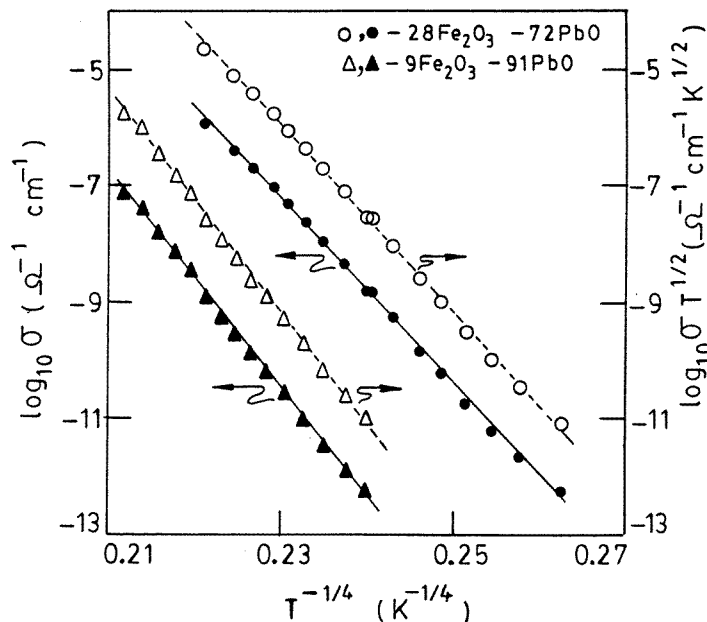
where  $\sigma_0$  and  $T_0$  are constants and  $T_0$  is given by

$$T_0 = \frac{19.44\alpha^3}{k_B N(E_F)} \quad (7)$$

where  $N(E_F)$  is the density of states at the Fermi level. On the other hand, variable-range hopping which takes correlation effects between the charge carriers into account predicts that [21]

$$\sigma = \sigma_0 (T_0/T)^{1/2} \exp[-(T_0/T)^{1/4}]. \quad (8)$$

A plot of logarithmic conductivity versus  $T^{-1/4}$  is shown in figure 4 for two glass compositions. A plot of  $\log_{10}(\sigma T^{1/2})$  versus  $T^{-1/4}$  is also shown in the same figure. The data are fitted to these models by the best-fit methods. The qualities of the fits are comparable for these two models. The values of the density of states at the Fermi level are obtained from the fits and are shown in table 2. It is seen (table 2) that the values of  $N(E_F)$  increase slowly with increase in the iron ion content in the glass compositions.

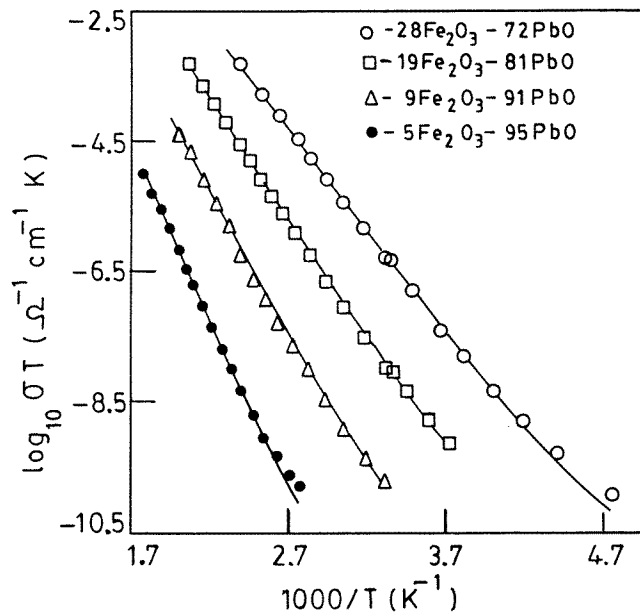


**Figure 4.** The plots of  $\log_{10} \sigma$  and  $\log_{10}(\sigma T^{1/2})$  as functions of  $T^{-1/4}$  for two glass compositions: —, best fit to equation (6); - - -, best fit to equation (7).

Schnakenberg [16] has considered a more general polaron hopping model where the optical multiphonon process determines the conductivity at high temperatures, while at low temperatures the acoustic one-phonon-assisted hopping process is operative. The conductivity in this model takes the form

$$\sigma \sim T^{-1} [\sinh(h\nu_o/k_B T)]^{1/2} \exp[-(4W_H/h\nu_o) \tanh(h\nu_o/4k_B T)] \exp(-W_D/k_B T). \quad (9)$$

This model predicts a temperature-dependent activation energy which decreases with decrease in the temperature and is consistent with the data presented in figure 1. Thus it appears that this model may be appropriate to explain the electrical data for the present glass systems. In figure 5 the experimental data are fitted to equation (9) by the best-fit method. The values of the parameters  $\nu_o$ ,  $W_H$  and  $W_D$  are listed in table 3. It is noted that the value of  $\nu_o$  is close to that estimated from the infrared studies [14]. The values of hopping energy decrease with decrease in the  $\text{Fe}_2\text{O}_3$  content in the glass compositions. Values of  $W_D$  are very small for all compositions. So, almost all the activation energy is attributed to the hopping energy.



**Figure 5.** Plots of  $\log_{10}(\sigma T)$  as a function of inverse temperature for the same glass compositions as in figure 1: —, best fits of the experimental data to equation (9).

#### 4. Conclusions

The temperature-dependent electrical DC conductivities of binary lead-iron glasses are presented. Analysis of the experimental data reveals that Mott's phonon-assisted hopping of the polaron between nearest neighbours is operative in the high-temperature range, while in the low-temperature region the variable-range hopping mechanism is active. Hopping between the two valence states occurs by a non-adiabatic process. The temperature dependences of conductivity and activation energy for all glass compositions are best explained by the small-polaron hopping model of Schnakenberg. The values of parameters obtained from the fits of these models are consistent with the glass compositions.

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